High Energy Density Electrodes *via* Modifications to the Inactive Components and Processing Conditions

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LBNL
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bat232

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Overview

Timeline

- October 1, 2018
- September 30, 2023
- 75%

Budget

- Total project funding
  - DOE share: 100%
  - Contractor share: 0%
- Funding for FY 2020
  - $290 k
- Funding for FY 2022
  - $400 k; 2/5 PI, 2/3 Res. Assoc.

Barriers and Technical Targets

- Barriers addressed
  - Fast charge:
    - 80% of Useable Energy in 15 min
  - Cycle life:
    - 1000 deep discharge cycles
  - High specific energy:
    - 350 Wh/kg – cell level
  - High specific power
    - 700 W/kg for 30 sec. – cell level

Partners

- Commercial
  - Arkema
  - Daikin America
- Public - DOE
  - AMO:
    - R2R National Laboratory Collaboration
  - FCTO:
    - Million-Mile Fuel Cell Truck Consortium
  - VTO:
    - Silicon Consortium, DRX Project, SSB Project

Relevance

Objectives

- To minimize the trial and error of electrode formulation and fabrication of any new material through the measurement of the most relevant physical properties of each component

Impact

- The saving of millions of research dollars in time and resources in the electrode fabrication of new battery materials.
- The saving of millions of research dollars by rapidly assessing the maximum performance capability of a new material.

What we now know

- To produce an electrode that coats well and dries without cracking starts with a slurry of a narrow viscosity range.
  - The viscosity is highly dependent on the high surface area of the carbon additive
  - One must arrive at a carbon concentration that leads to the proper slurry viscosity and electrode electronic conductivity
- During drying, the fully extended dissolved binder will contract.
  - Without solids, the contraction leads to a polymer film that does not adhere to the current collector.
  - Too low a solids to binder ratio allows the binder to contract too much during drying, reducing contact points with the current collector and detachment
  - Too high a solids to binder ratio also results in too few contact points between binder and current collector.

The carbon and binder contents greatly impact the rheology of the slurry and performance of the electrode. There is no guidance on how to arrive at the optimum ratio for a new material.

Progress Measures FY ’21-22

Date	Milestones and Go/No-go Decisions	Status
June 2021	Investigate the amount of solvent in the slurry, *i.e.* the viscosity, on the impact of laminate properties (cracking, adhesion, cohesion).	Met
[redacted]		
September 2021	Complete cycle life testing of laminates with improved coating processes.	Met
	[redacted]	
December 2022	Assess the properties of binder-carbon laminates.	Met
	[redacted]	
March 2022	Use ion polishing to cross section electrodes, followed by SEM and EDS to investigate carbon and binder distribution.	Met
		[redacted]

Progress Measures FY ’22-23

Date	Milestones and Go/No-go Decisions	Status
June 2022	Determine at what level dissolved binder in the mixing solvent (NMP) can prevent NCM particle breakdown.	On schedule
[redacted]		
September 2022	Use tomography of ALS to better understand the impact of solvent quantity on laminate properties.	On schedule
	[redacted]	
December 2022	Complete the measurement of electronic conductivity of laminates with and without NCM 632, and different loadings of carbon and binder.	On schedule
	[redacted]	
March 2023	Initiate a new round of studies using a lower molecular weight binder.	On schedule
		[redacted]

Approach to Address Electrode Function as it Pertains to Electrode Formulation

- Initial investigations were focused on process conditions
  - Investigated macroscopic processing conditions on mechanical and power performance properties.
  - Investigated aspects of mixing, including:
    - Order of, speed, duration, solvent level, stand time prior to casting, and drying rate
    - Investigated different drying temperatures
    - Performed XRD to establish crystal structure of polymer as a function of drying temperature
    - And investigated the mechanical properties of the polymer as a function of crystal structure and carbon content.

- Updated approach toward pushing the inactive fractions to their minimums
  - Focusing on low carbon-binder electrodes (which allows us to better identify aggregates and the phenomenon of aggregation.)
  - Minimizing anthropogenic influences on process conditions by automating most process steps
  - Incorporating in-line particle size analyzer to measure critical slurry properties as a function of mixing speed and time
  - Constructing a remote controlled coating system to utilize the ALS and a confocal microscope to examine tomography during drying.

- Collaborate with other programs focused on improved manufacturing
  - Apply results to other VTO programs including DRX, NMO, Si, and Solid State Battery programs
  - Coordinate work with DOE AMO R2R National Lab Collaboration
  - Coordinate work with electrode fabrication component of the Million Mile Fuel Cell Truck (M2FCT) Program

General Philosophy

- The investigation of a new material starts at the bench scale with a small amount of material.
- It is critical that researchers have guidance on how to turn a small amount of powder into a highly functioning electrode with minimal resources.

Our goal is to codify the formulation process of battery slurries that will lead to easily coatable slurries, uniform laminates, ultra high energy densities, and optimally performing electrodes in a single iteration.

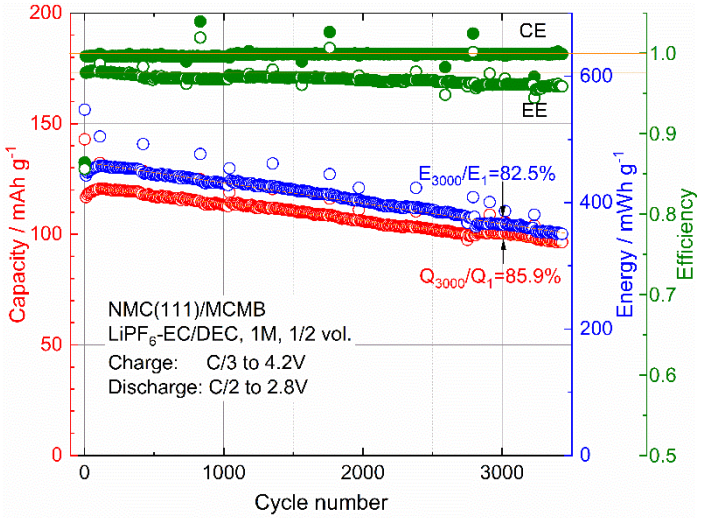
Technical Accomplishments and Progress

Cumulation of Project Accomplishments (blue are the most recent)

- Carbon additive plays several roles in Li-ion electrodes
  - The obvious:
    - It provides electronic conductivity to the surface of the cathode material to promote conduction along the surface of the active material and facilitate charge transfer
    - It assists in particle to particle electronic charge conduction through the electronically insulating polymer component holding the particles together.
  - The aggregation of high surface area carbon is critically important to:
    - the shear thinning property of the slurry that allows for high speed slot die coating,
    - the promotion of open porosity in films
  - Mixing the carbon with the active material first, promotes good contact and limits the breakage of the active material during periods of intense mixing.
  - The carbon induces a highly porous electrode structure, critical for reducing laminate contraction during drying and enhancing electrolyte transport in the finished electrode
- More binder can result in less adhesion.
- The amount of solvent in the slurry has a significant influence on the properties of the final electrode.

It should be noted that all research was performed at the high loading of 5 mA/cm^2 and limited to one set of materials: NCM 622, Denka Black, and PVdF HSV 900 (Arkema).

Gr/NCM cell



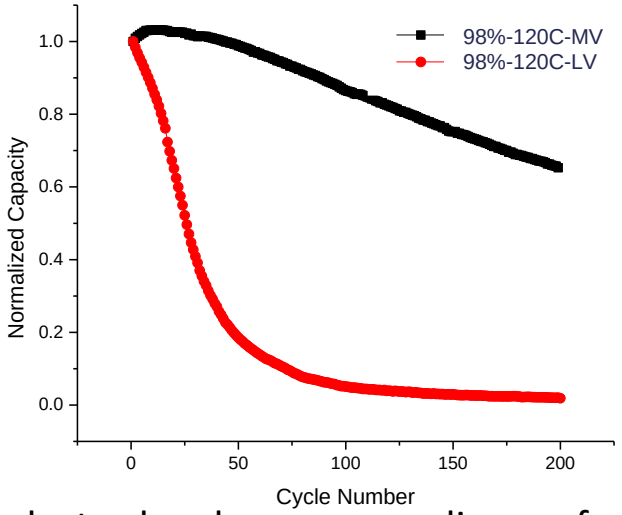
After years of experience, we can make excellent electrodes of graphite and NMC.

Can we achieve a fundamental understanding of why this system performs so well that we can translate it to other active materials?

Technical Accomplishments

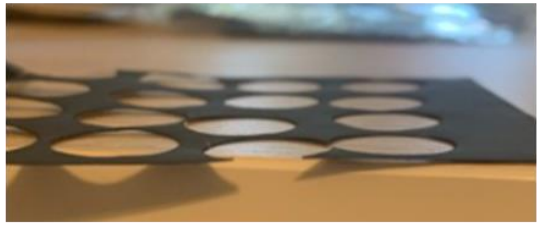
Solvent content

	Adhesion (Nm-1)	Cohesion (Nm-2)	Slurry Viscosity
98% MV	0.00106	0.00213	0.52
98% LV	N/A	0.00071	0.16
98 % HV	N/A	N/A	N/A



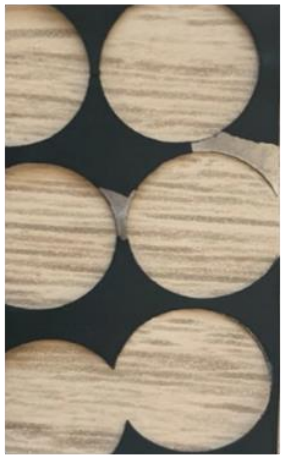
- LV electrodes show poor cycling performance
- MV electrode shows good cycling performance
- HV electrodes couldn't be punched without complete delamination (cycling could not be performed.)

Low Viscosity



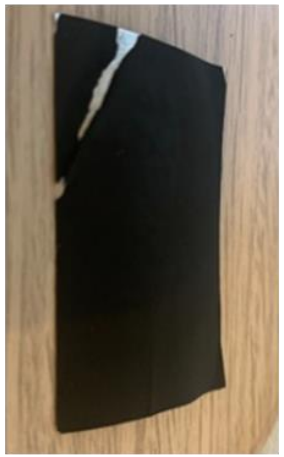
- Good bendability
- No delamination
- High adhesion
- Low cohesion

Moderate Viscosity



- Good bendability
- Delamination during electrode punching
- Relatively higher adhesion/ cohesion

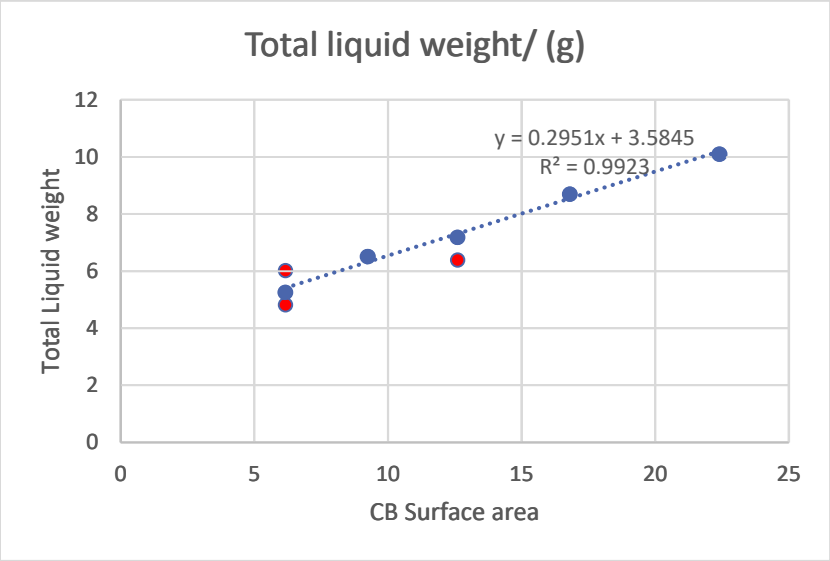
High Viscosity

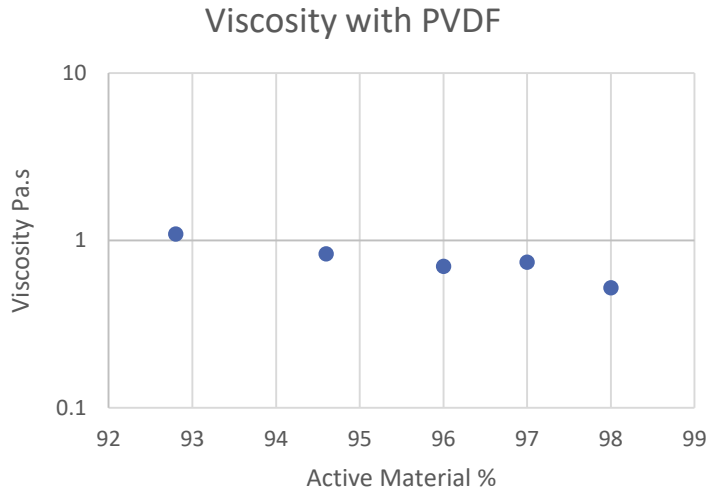


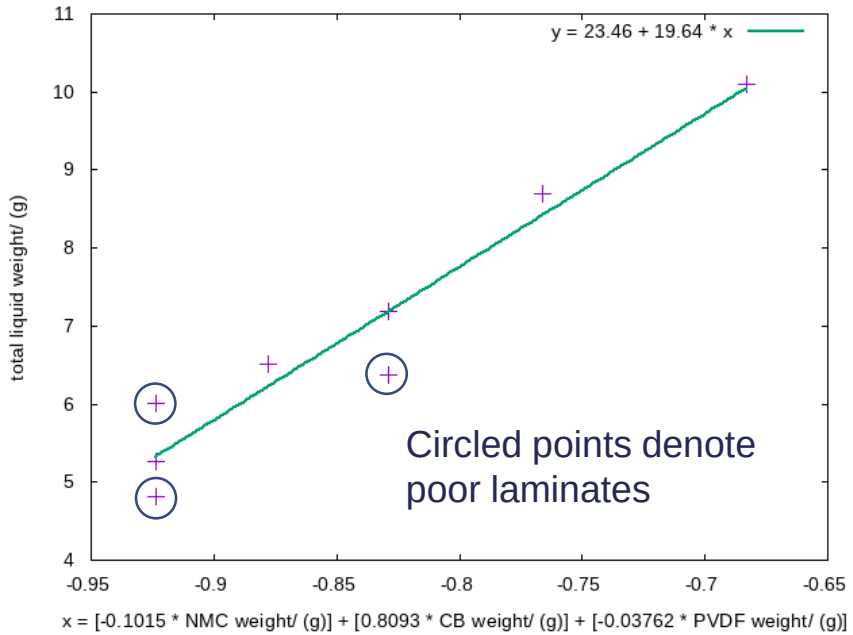
- Delamination before electrode punching, hence no cells were made
- Cracking observed during bending
- No adhesion/cohesion data

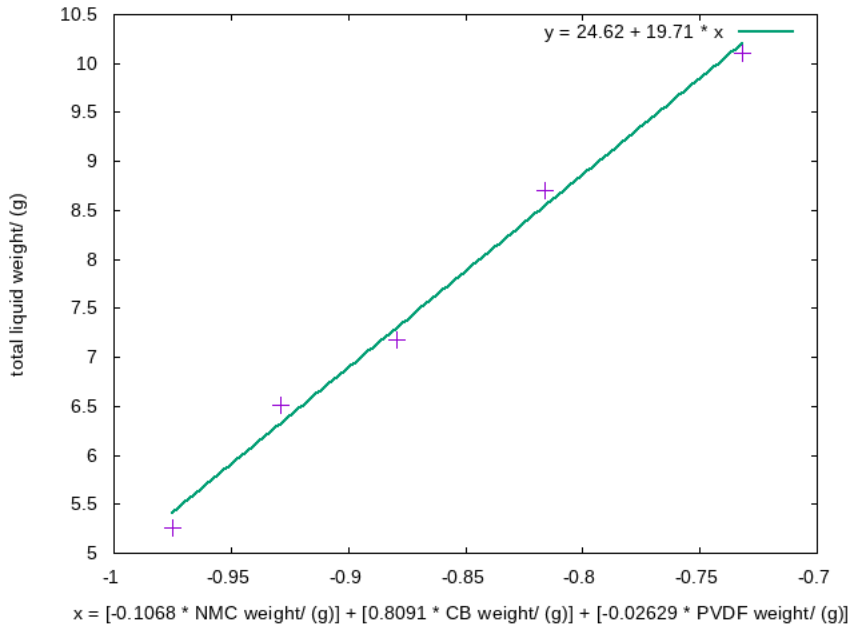
Technical Accomplishments*

Solvent content









The "magic" of electrode coatings appears to be in the solvent content!

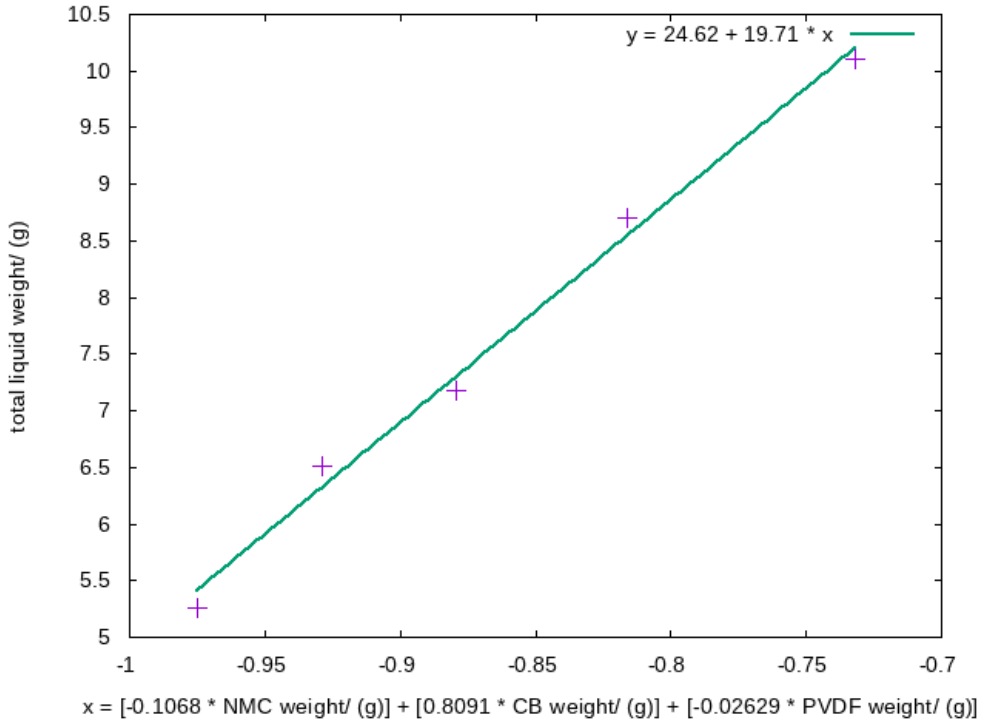
For this materials set, the amount of solvent for a good electrode was linearly coordinated to the total surface area of carbon.

This did not result in exactly the same viscosity.

Slight variations from the ideal solvent content lead to either poor adhesion and/or cohesion.

Technical Accomplishments*

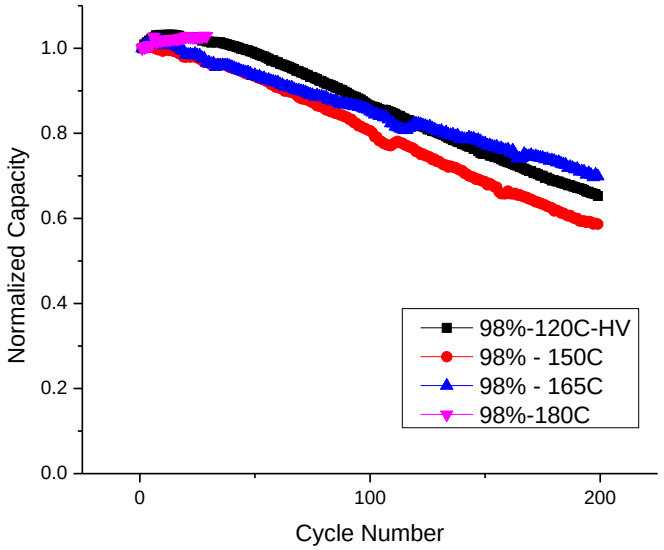
Solvent content

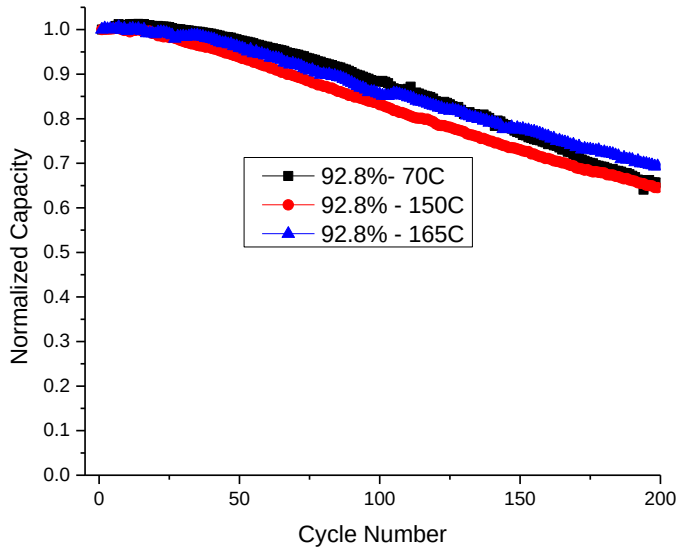


Through principle component analysis (a subset of machine learning) we were able to derive a relationship between the amount of solvent and the other components in the system.

Technical Accomplishments

5 mAh/cm^2 loading



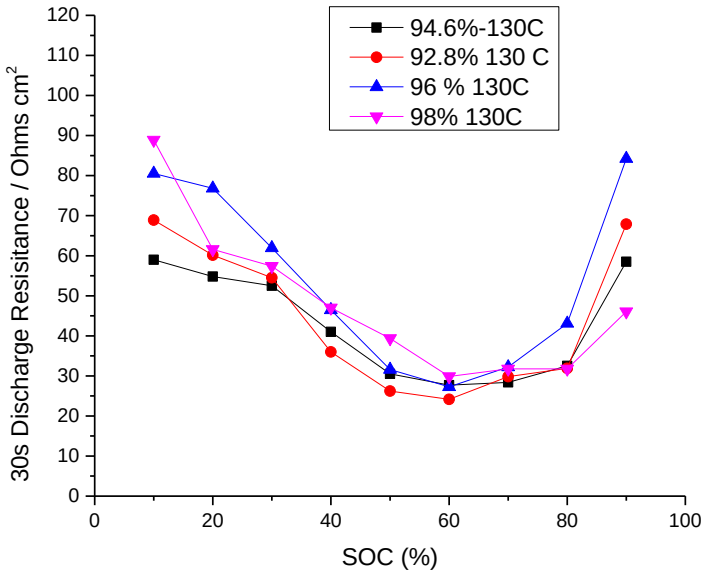


- Data shows that electrodes made at 92.8 % and 98 % active material (NMC 622) with a carbon : binder ratio of 45:55 all cycle similarly.
- The electrodes dried at 165 ^{o}C shows slightly better capacity retention than the others
- The capacity retention after 200 cycles is around 70% which is not ideal
  - Other research is starting to point to the pressure in the coin cell as contributing to capacity fade.
  - The pressure can sometimes be too high or too low, depending on the adjustments made to the cell.

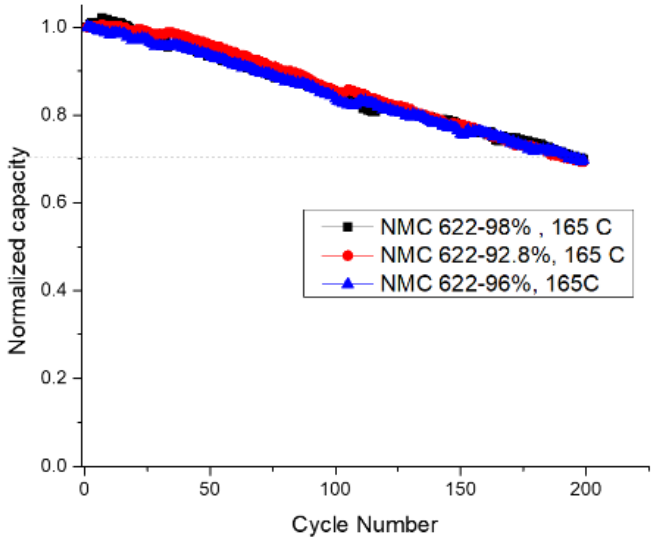
Technical Accomplishments and Progress

No cracking, consistent performance, fast drying (165^{o}C); no matter the quantity of inactives,

HPPC Data



Cycling Data



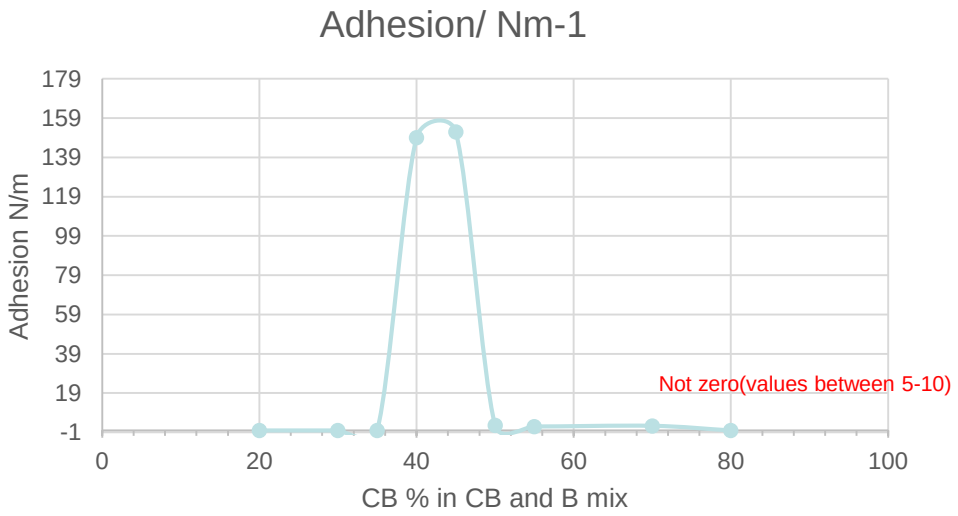
Can we go lower?

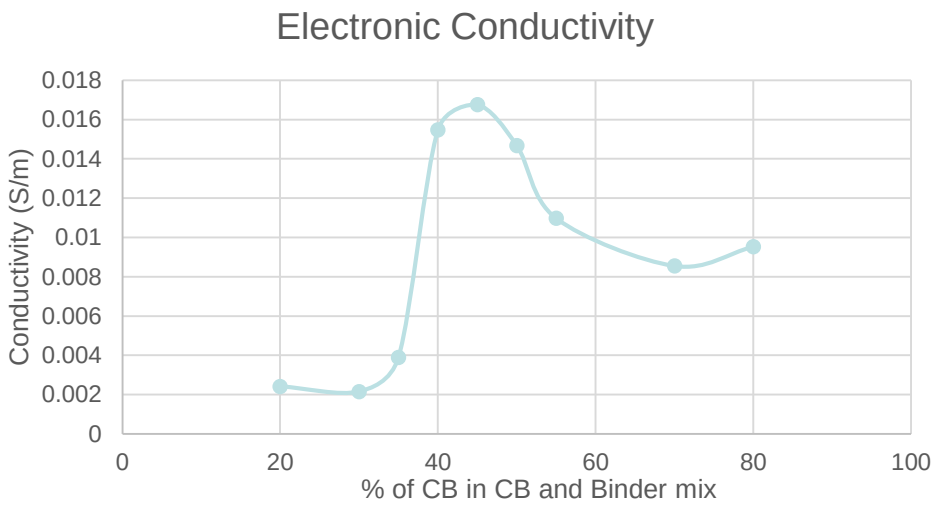
Technical Accomplishments and Progress

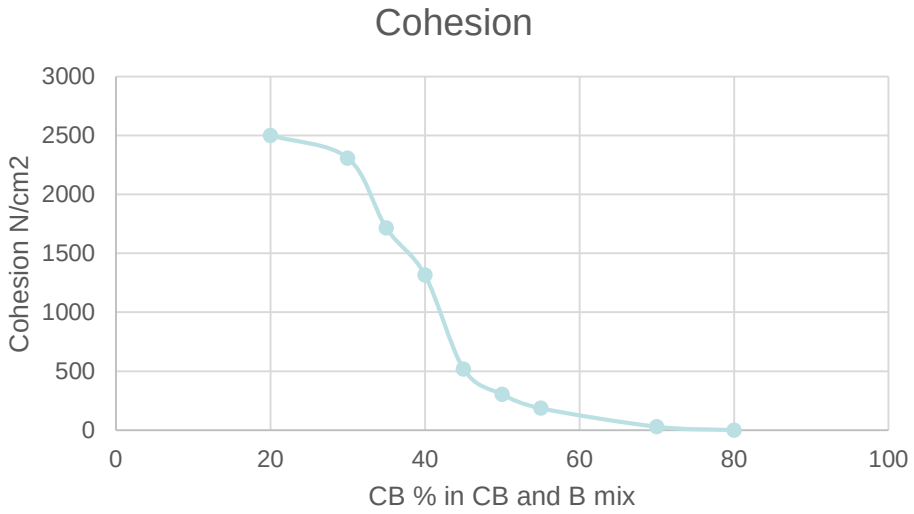
Previously, we focused primarily on process conditions, we have now turned our attention to formulations in an attempt to understand the limits of the total amounts of binder and carbon, by focusing on the pairwise interactions between carbon-and-binder, active material-and-carbon, and active material-and-binder with the goal of deriving *apriori* the amounts needed to prepare high-capacity-density, high-performing electrodes.

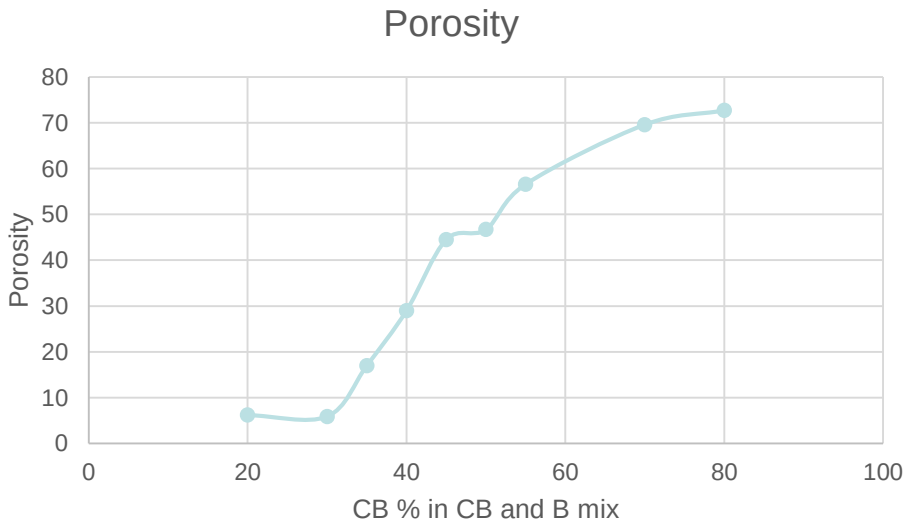
Technical Accomplishments and Progress*

CB:B ratio: A delicate balance









There is a <u>narrow window</u> of CB:B where adhesion is good.

- Too little carbon and there is too much contraction during drying
- Too much carbon and there are not enough contact points between binder and current coll.

Cohesion and porosity are inversely related – you need both for good electrode performance.

- Stiff, chains of carbon aggregates create a very open structure.

Poor adhesion and cohesion reflected in peak in electronic conductivity.

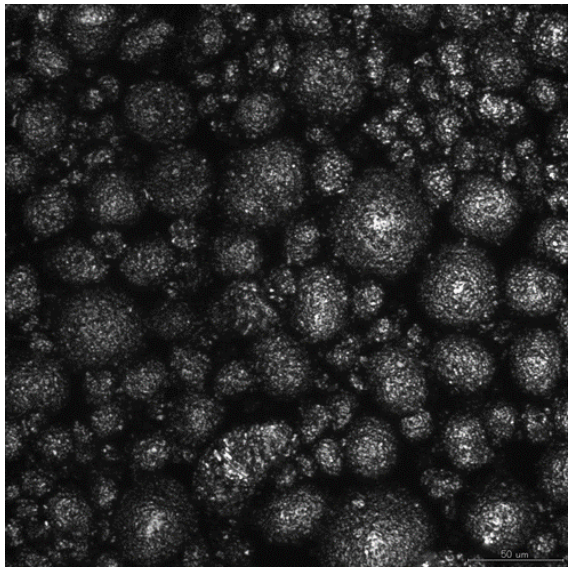
Technical Accomplishments and Progress

Where we left off last year.

- ❑ Mixing order matters
  - The mixing of carbon and NCM first helps prevent particle breakdown.

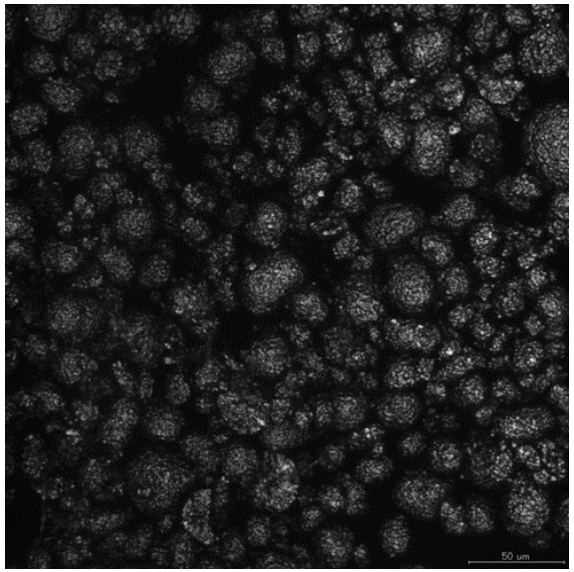
Images from a confocal microscope

(AM + C) + B



Same scale

AM + B



No carbon

Low amounts of carbon and binder require mixing of the active material with the carbon first to prevent breakdown of the active material during mixing.

This limits our ability to investigate NCM:Binder relationships at low binder contents.

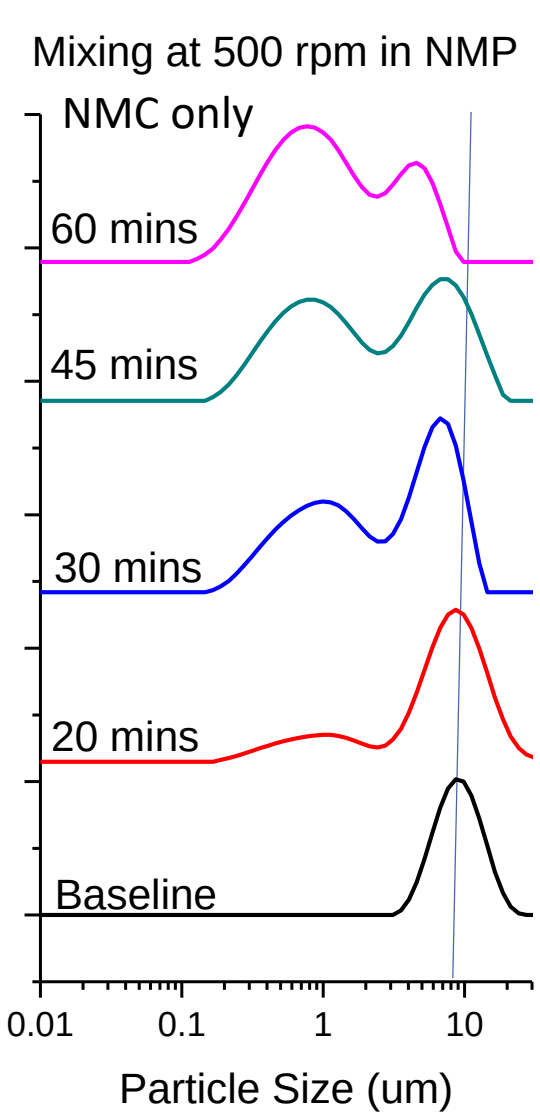
Technical Accomplishments

- Mixer and particle size analyzer in a continuous loop.

Homogenizer

Particle size analyser

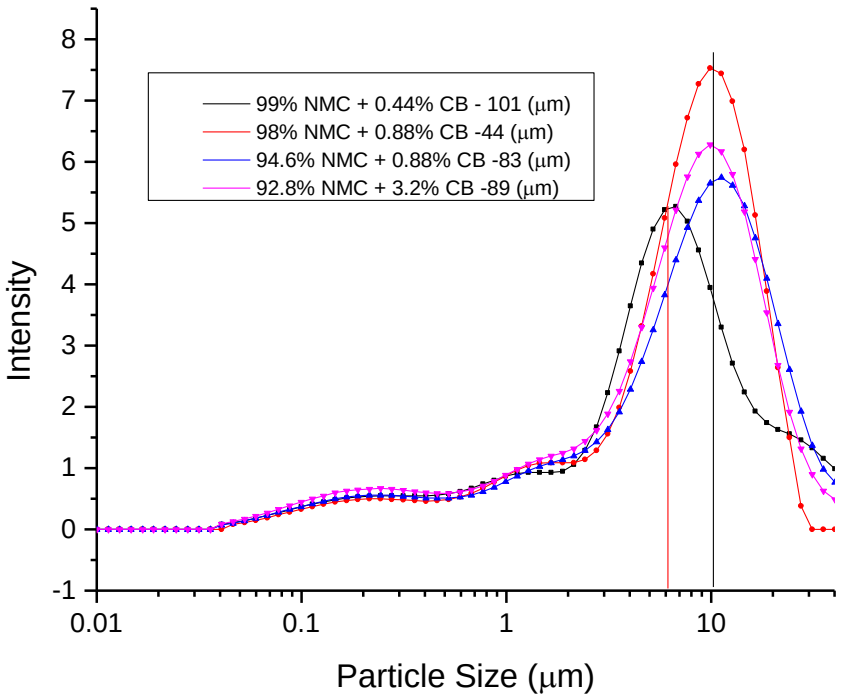
Technical Accomplishments*



NMC mixed alone in solvent *vs*. time

- Impact on particle size in 20 min.

NMC mixed with different levels of carbon black in solvent for 25 min.



As little as 0.8:98 CB:NMC can stop NMC particle breakdown.
Below 0.5:99 exhibits NMC breakdown.
Does this contribute to the poor adhesion and cohesion?

Technical Accomplishments

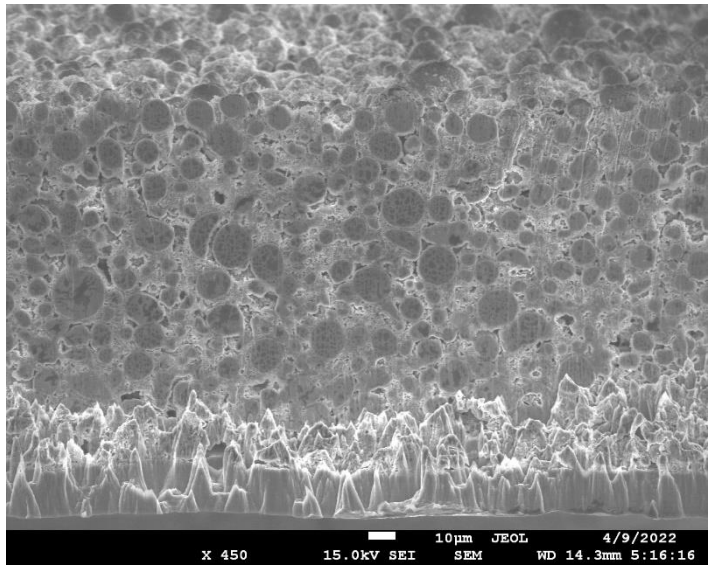
99% Electrodes

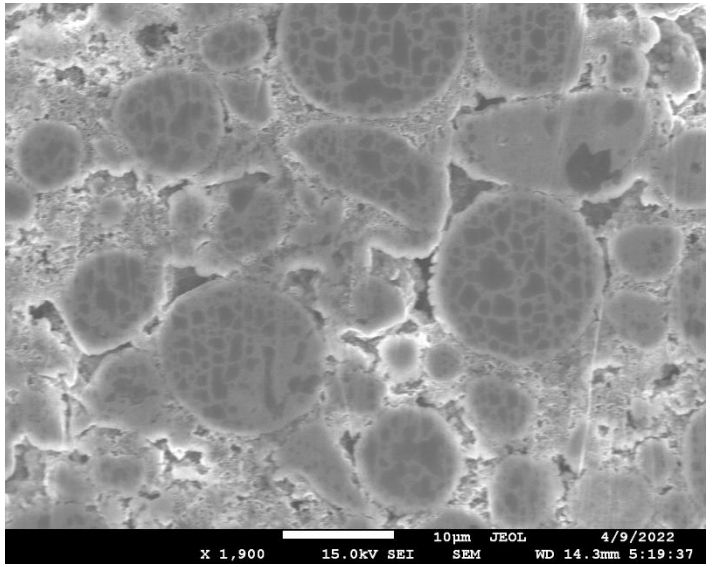
- Electrodes can be made with ~5 mAh/cm^2 loading with no mud cracking up to 180 ^{0}C
- However, the electrode delaminates during calendering
- Between the delaminated electrode and the current collector, dry powder that could be wiped off as seen on the picture

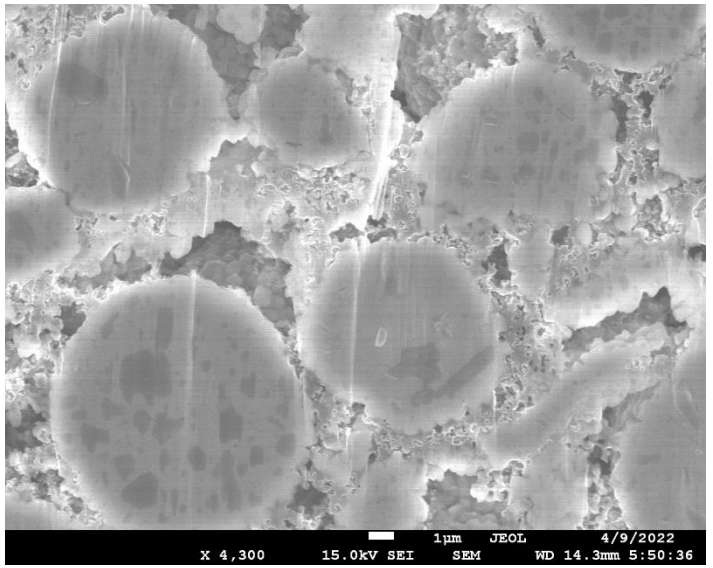
- It is possible these electrodes did not coat well due to breakdown of the cathode material during mixing.

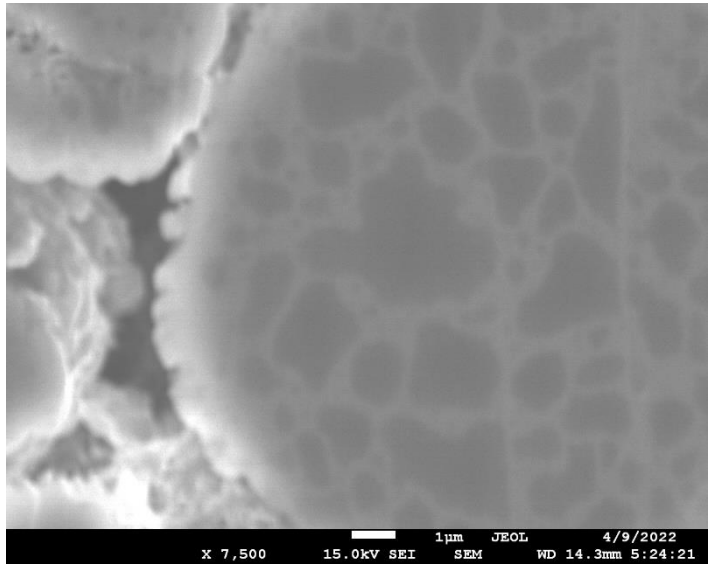
Technical Accomplishments and Progress

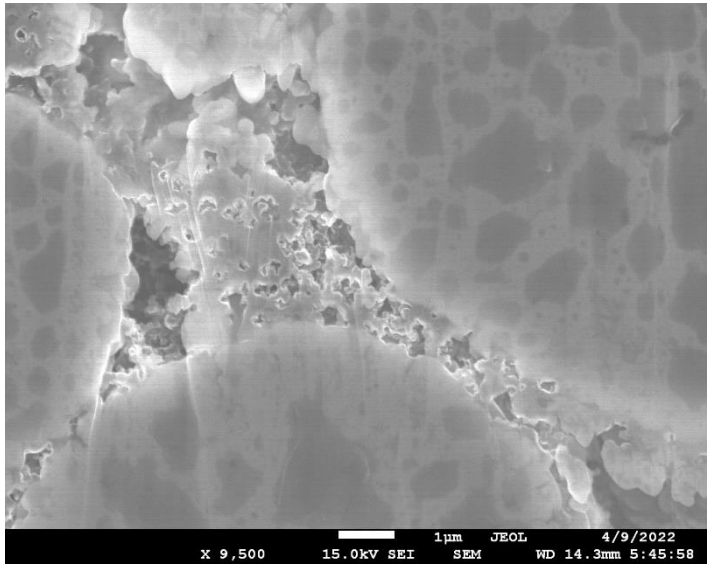
Ion polishing combined with SEM











- Zoomed into the secondary particles to see the primary particles
- The carbon and binder content was too low to chemically detect with EDS.
- Will attempt to map it out with help using the ALS.

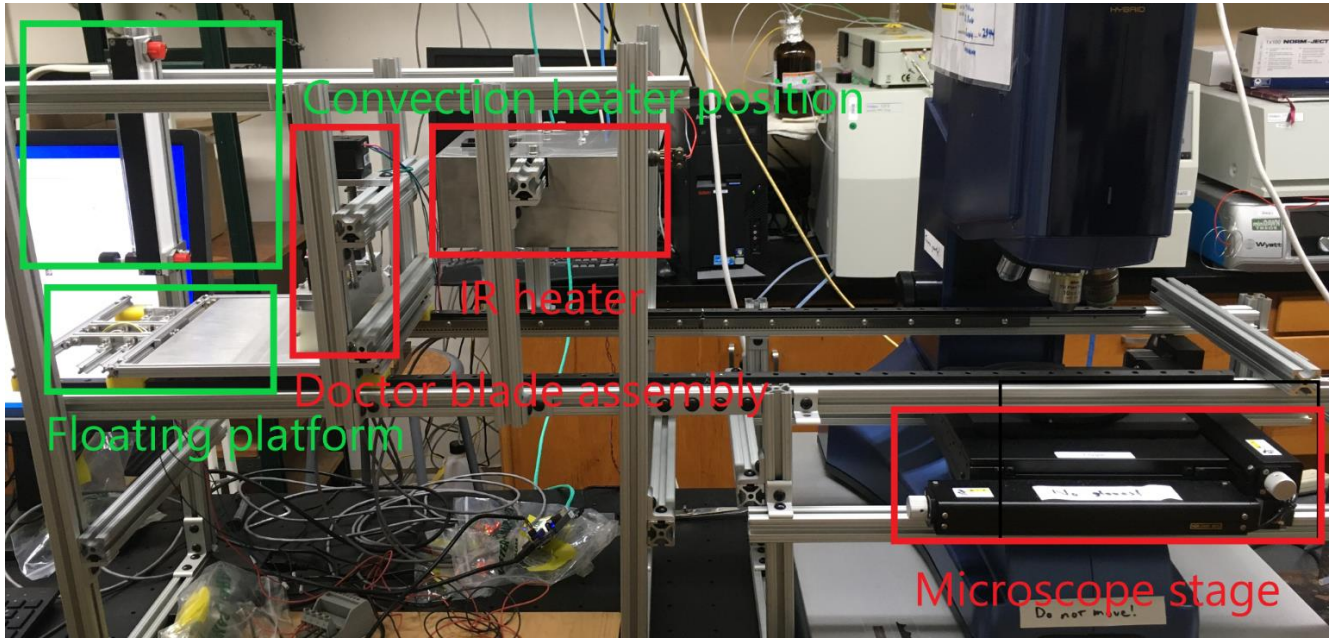
Technical Accomplishments and Progress

Automated miniature electrode fabrication system

- Designed to interoperate with
  - confocal microscope (focusing performed by microscope stage movement)
  - ALS hard X-ray tomography beamline (radiography only)

- Includes custom, programmable
  - dynamically adjustable doctor blade
  - IR heater unit
  - convective heater unit (undergoing final assembly)

- Controllable through Ethernet or USB connections
  - Client programs can use a wide range of programming languages



We look forward to using this set-up to visualize particle aggregation during drying of laminates.

Responses to Previous Year Reviewers' Comments

Mostly positive feedback; here we address the more critical comments

- One reviewer stated "*The imaging approach could be improved with some synchrotron methods, which can give much higher spatial resolution and chemical sensitivity*." We have developed an apparatus that will allow us to remotely perform coatings in the beamline hutch so that we can monitor the tomography during drying.
- One reviewer suggested that "*the PI investigate carbon materials with different properties, e.g., surface area, crystallography, surface functional groups, etc., along with different binder materials."* Once we have completed our present analysis we plan to do just that.
- One reviewer commented that "*the weakness of this project is the need and relevance of this activity in a national laboratory environment*." We would argue that such an effort is necessary as several researchers that specialize in material synthesis have no guidance in how to make a good electrode to adequately test their material.

Collaboration and Coordination with Other Institutions

- This research is conducted among a significant amount of parallel research in electrode processing that is funded by VTO, AMO, and FCTO.
  - FCTO: We attend a biweekly meeting where the discussion is focused on issues of casting and drying of electrode films for fuel cells in the Million Mile Fuel Cell Truck Program
  - AMO: We participate with 4 other national labs (ANL, NREL, ORNL, and SNL) in studying the science of high speed roll-to-roll manufacturing
  - VTO:
    - We are responsible for optimizing electrode performance of DRX materials
    - We are assisting the Si Consortium in trying to make quality electrodes of pure silicon particles
    - We are assisting in the effort to develop a buffer layer on lithium in the Solid State Battery program
- There are several semi-monthly deep-dive meetings that result in in-depth conversations and data exchange on a broad range of electrode manufacturing topics that typically point to particle level interactions.
- We consult and exchange materials with companies and universities, like Arkema and BYU.
- We consult with experts internally at LBNL, including members of the Molecular Foundry, ALS, and the Computational Research Area.

Collaboration with this multitude of institutions is much more beneficial to the electrode fabrication community than a collaboration with a single company could ever be.

Remaining Challenges and Barriers

The project objective is to understand the underlying physics to formulating high-loading, high-energy density electrodes.

- Remaining questions:
  - What is the minimum value in adhesion necessary to punch/slice an electrode? (once the cell is assembled under pressure, the need for adhesion diminishes)
  - We need to assess long-term cycleability. (The electrodes on test are in half cells where the cycleability can be shortened by changes in the lithium counter electrode.)
  - Why are slight changes in solvent content having such an impact on electrode performance?
  - Why does 165 ^{o}C in our drying chamber appear to be the best for cycleability?
  - Is there a dissolved binder fraction that would limit particle breakdown of NCM if no carbon was present?
  - All of our results are a function of the active material, carbon, and binder properties. We need to spend more time examining different active materials, different carbons, and polymers of different molecular weights.
    - *E.g.*, Is the magical solvent content just a function of the carbon surface area or are there other aspects of the carbon to consider?

Proposed Future Research

- Rest of FY22
  - Investigate binder loading in the solvent to determine if any level is capable of preventing NCM particle breakdown.
  - Use the advanced light source and our remote laminate casting system to visualize the impact of solvent content on laminate formation.
    - This includes the effect of drying at different temperatures
  - Evaluate different combinations of binder and carbon in very high active material content formulations to understand how the three components combine to give electronic conductivity, adhesion, and cohesion.

- FY23
  - Investigate the source of energy fade in high loading cells
    - Including the impact of cell pressure on life.
  - Formulate cells of high loading and low adhesion to the current collector and define lowest tolerable level of adhesion.
  - Evaluate the replacement of the high molecular weight PVdF with a lower molecular weight form.
  - Evaluate the replacement of the Denka Black with another high surface area carbon.

Any proposed future work is subject to change based on funding levels.

Summary Slide

- General Premise
  - Binder is critical for binding the active material particles together and to the current collector.
  - Carbon additive is necessary to conduct electrons throughout the surfaces of the active material
    - As a surface agent, it does not need to be thick and hence small carbon particles are used and added to the active material in the slurry
  - Since, ultimately, Li-ions must pass through the active material interface, the binder need only appear between particles and the carbon on the surface should only partially cover the active material surface.
- Key points from this presentation
  - The “right” solvent content in the slurry leads to uniform films that coat well, dry without cracking, and possess good adhesion and cohesion.
  - The “right” solvent content, for a given set of materials, is proportional to the amount of carbon in the mixture.
  - The “right” solvent can resolve variability in electrode uniformity, and mechanical and electrochemical properties..
  - If you have cell variability in your lab, you may want to start here.
  - There is a narrow window of the carbon to binder ratio that leads to good adhesion, good cohesion, electronic conductivity and good porosity.
  - To mix the three components together, the carbon must be present when the active material is present - it prevents the pulverization of the active material.
  - For this material set, there must be at least 0.5:99 carbon:NCM; below 0.5:99 C:NCM, there is evidence of NCM breakdown within 20 minutes of mixing.
  - We can produce high loading laminates of 99% active material, but the active material is pulverized and the laminate has poor adhesion and cohesion. We were unable to transfer the laminate to a cell.
  - We were able to obtain electrode cross sections with an ion beam polisher; we were not able to detect the low concentration of carbon and binder. We designed a remote casting system that will allow us to use the advanced light source for examining drying *in operando* and hopefully detect the carbon and binder.

Critical Assumptions and Issues

Although our results carry wide ranging implications for many who make electrodes, there are limitations of extrapolating our results to large-scale manufacturing

- Many of our results are based on the mixing produced by a high-shear homogenizer. Such an instrument mixes well on a scale of milliliters of slurry. The results may not be identical with the large scale mixing systems found in industry.
- Drying conditions play a critical role in drying rate, which, in turn, dictates crack formation. The conditions in our oven may not be consistent with those of high speed roll-to-roll coating/drying lines.
- All of the electrodes are tested in a planar geometry, impacts of rolling around a mandrel are likely neglected.